Equilibrium Gas-Oil-Ratio Measurements Using a Microfluidic Technique

Robert Fisher, Mohammad Khalid Shah, Dmitry Eskin, Kurt Schmidt, Anil Singh, Shahnawaz Molla, and Farshid Mostowfi*

Schlumberger DBR Technology Center, 9450 17th Ave., Edmonton, Alberta, T6N 1M9, Canada

Thermodynamics of hydrocarbon fluids

Crude oils are characterized based on their compositional as well as thermo-physical properties. Figure S1a shows the *PT* diagram for a typical "black oil". The thick solid line depicts the phase boundary of the fluid. The phase boundary separates the single phase region from the two phase region. Line ABC shows an example of constant temperature pressure depletion for the fluid, which is what happens when the fluid travels from a reservoir to the surface through the well. Point A represents the reservoir conditions, i.e. single phase liquid at a pressure above saturation pressure. Once the fluid travels up towards the surface, local pressure drops to the saturation pressure shown as point B. At a pressure below saturation pressure, a gas phase emerges from the fluid and a two phase fluid is formed.

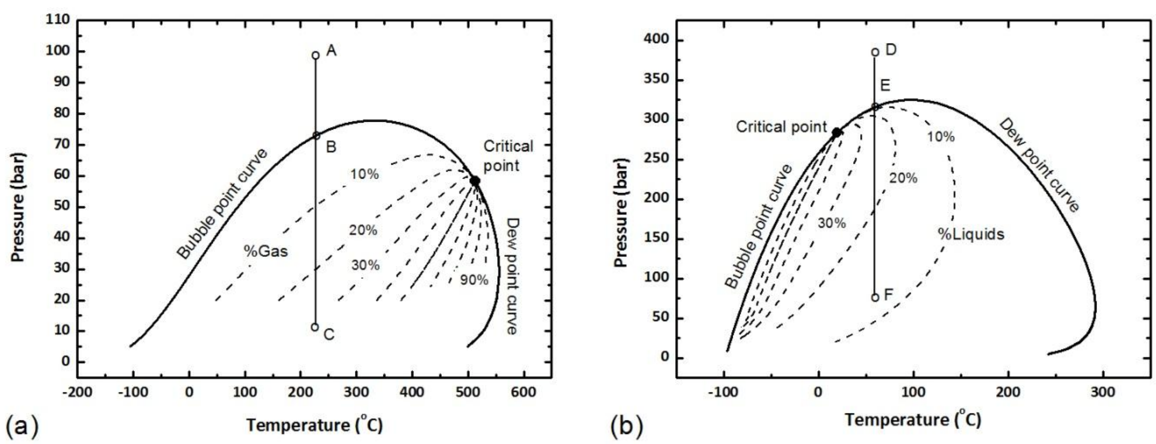

Figure S1. Typical *PT* diagrams for (a) a black oil and (b) a gas condensate

Figure S1b shows a typical *PT* diagram for a different form of reservoir fluid call "gas condensate". A reservoir fluid is classified as gas condensate when the reservoir temperature is on the right-hand-side of the critical point. At point D, the fluid is a supercritical gas. However, such fluids contain considerable amount of heavy components that may become insoluble at a lower pressure. At point E, the fluid reaches a saturation state, where heavier components condense in to a liquid form. Figure 1 shows isothermal depressurization processes for both fluids.

Experimental procedure for the direct flash and the pycnometer flash

Direct flash. The procedure for the direct flash was similar to that for the microfluidic flash. However, to control the flow accurately, a fine control valve was connected to the sample side valve of a pressurized sample bottle. The valve required periodic adjustments to maintain a slow flowrate. The input side of flow through glass trap was then connected to the fine control sampling valve. The output side of the flow through glass trap was then connected to the gas meter.

Pycnometer flash. An evacuated, pre-weighed pycnometer was connected to the sample valve of a pressurized sample bottle. The sample valve on the pressurized sample bottle was then slowly opened to allow sample to fill the pycnometer valve. Once pressure stabilized, the pycnometer valve was slowly opened to allow a sub sample to be collected within the pycnometer. The sub sample within the pycnometer was then removed from the sample bottle and connected to the gas meter. All lines as well as the gas meter were then evacuated with a vacuum. Once the evacuation was sufficient, the system was isolated from the vacuum and allowed to rest to determine the presence of any leaks. Once the system was deemed to be closed, then the flash was commenced. The flash began by slowly opening the pycnometer valve to allow the sample to flow through the liquid glass trap at rate that would only allow the vapor portion to enter the gas meter. This process was allowed to continue until system and pycnometer depressurized. The vapor collected within gas meter was then re-circulated through the liquid in order to reach equilibrium. The "re-circulation" configuration would only allow the vapor to circulate while the liquid remains within the pycnometer. Once the re-circulation was completed, the vapor volume was then recorded from the gas meter. A sub sample of the vapor was removed from the gas meter and analyzed for composition. The flow through glass trap was then weighed as well as the pycnometer to determine the liquid mass. The liquid was then analyzed for density and composition. The measurements are converted to Standard Conditions (1 bar and 15.5°C) and the GOR was calculated.

Mass transfer in segmented flows

A detailed mass transfer modeling and evaluation of deviations from equilibrium in microchannel slug flows is given in the recent paper of Eskin and Mostowfi.[1] Let us present a brief analysis of this problem. For the sake of simplicity, we will consider a micro-channel of a round cross-section. Note that the mass transfer in a microchannel of a rectangular cross-section is not expected to be significantly different.

A system, composed of a bubble surrounded with two liquid slugs is sufficient for our analysis. A bubble moves with the velocity U_B. The velocity distribution across the liquid slug is parabolic except a region in the bubble cap vicinity. It is convenient to introduce a coordinate system moving with the bubble velocity. In this system, the bubble is immobile while the liquid film moves in the opposite direction. Then, a clearance between the bubble and the wall is a channel connecting the slugs on the different sides of the bubble. The slug vortex motion can also be easily imagined in this coordinate system. The intensive mixing within the slug, in the case when the capillary number is below the critical value, allows assuming a uniform dissolved gas concentration c_0 over the slug volume. This concentration exceeds the equilibrium concentration of the dissolved gas c_s. Only the gas-liquid interface is characterized by the equilibrium concentration c_s. This concentration can be easily calculated (e.g., by the equilibrium flash method) for a given channel cross-section. The local pressure is determined assuming that the pressure distribution is linear.[2-4] Due to a large outer surface area of the microchannel, the temperature can be assumed constant along the entire channel.

The concentration difference c_0-c_s characterizes deviation of the system from equilibrium. To avoid a dependence of equilibrium characteristics on absolute concentration values, Eskin and Mostowfi[1] suggested the following phase equilibrium criterion:

$$\Delta = \frac{c_0 - c_s}{c_0} \tag{S1}$$

The bubble – liquid mass transfer should be considered for two different regions: 1) liquid – bubble cap; 2) liquid – cylindrical bubble section. The mass transfer rate in the first region is determined by the vortex intensity. For engineering calculations, a bubble cap shape is usually assumed to be semi-spherical. The Higbie's penetration model can be used to calculate the mass transfer coefficient in this region.[5] However, we are only interested in achieving equilibrium at the exit of the channel, where the void fraction is significant and the contribution of the bubble caps to overall mass transfer is insignificant. Therefore, the analysis of mass transfer in our GOR measurements system can be limited to the second region (liquid – cylindrical bubble section).

We can now formulate the mass balance equation for the slug and express the dissolved gas concentration change along the microchannel as follows:

$$\frac{dc_0}{dx} = -\frac{q_s}{U_B W_s} \tag{S2}$$

where q_s is the total mass flux from the liquid to the bubble and W_s is the slug volume.

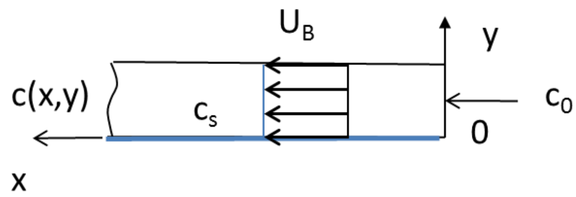

Fig.S2 Computational diagram for mass transfer in a liquid film

Assuming that the liquid film thickness is small compared to the microchannel radius, the mass transfer model for this region can be reduced to solving the advection-diffusion equation:

$$\frac{\partial c}{\partial x} U_B = D \frac{\partial^2 c}{\partial y^2} \tag{S3}$$

where c is the dissolved gas concentration in the liquid and D is the molecular diffusivity of the dissolved gas in the liquid.

The boundary conditions for Eq. S3 are (see Fig. 2):

$$c = c_0 \quad \text{at} \quad x=0$$

$$c = c_s \quad \text{at} \quad y=0 \tag{S4}$$

$$\frac{\partial c}{\partial y} = 0 \quad \text{at} \quad y = \delta$$

Equations S2-S4 describe mass transfer in a segmented flow. Let us, instead of solving the model equations accurately, derive an order-of-magnitude estimate for the equilibrium length of the channel.

The mass flux from the fluid to the bubble is calculated as:

$$q_s = 2\pi \left(R_c - \frac{\delta}{2}\right) U_B \int_0^\delta \left(c_0 - c(L_B, y)\right) dy \approx 2\pi R_c U_B (c_0 - c_{\,m}(L_B))\delta \tag{S5}$$

where R_c is the channel radius, L_B is the length of the cylindrical bubble section, and $c_{\,m}(L_B)$ is the average dissolved gas concentration at the bubble-wall clearance outlet.

Assuming that the concentration of dissolved gas in a fluid during the transportation through the bubble-wall cylindrical clearance does not change significantly, Eq. S3 allows writing the following relation:

$$\frac{c_0 - c_m(L_B)}{L_B} U_B \sim D \frac{c_0 - c_s}{\delta^2} \quad \text{(S6)}$$

Combining the above equations, we can write:

$$q_s \sim 2\pi R_c L_B \frac{D}{\delta}(c_0 - c_s) \quad \text{(S7)}$$

Substituting Eq.S7 into Eq.S2 we obtain:

$$\frac{d(c_0 - c_s)}{dx} \sim -\frac{2\pi R_c L_B}{U_B W_s} \frac{D}{\delta}(c_0 - c_s) \quad \text{(S8)}$$

Note that the equilibrium concentration c_s was introduced under the differentiation sign, because it is assumed that in a segmented flow, the system approaches equilibrium fast enough to neglect changes in c_s along the length needed for the equilibration.

Let us assume:

$$\frac{d(c_0 - c_s)}{dx} \sim \frac{c_0 - c_s}{X} \quad \text{(S9)}$$

where X is the equilibration length. We can write:

$$\bar{X} = \frac{X}{R_c} \sim \frac{U_B W_s}{2\pi R_c^2 L_B} \frac{\delta}{D} \approx \frac{1}{2} \frac{1-\varepsilon}{\varepsilon} \frac{U_B \delta}{D} = \frac{1}{2} \frac{1-\varepsilon}{\varepsilon} Pe \quad \text{(S10)}$$

where Pe is the Peclet number for the mass transfer in the liquid film, ε is the gas holdup.

References

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